This tactic provides a brief description of some potential spill substances and their expected effects on tundra vegetation and soils. Data are limited, and much of what is known about the effects of spills to tundra is the result of spills or field experiments in this region. The companion manual to this publication, "Tundra Spill Cleanup and Remediation Tactics: A Study of Historic Spills and Literature" (Behr-Andres, 2001), provides the scientific basis for decisions on tactics to be used for a particular spill scenario.

This discussion focuses on hazardous substances that are produced, extracted, or used in the production or extraction of oil and gas in Alaska's arctic oilfields. Hazardous substances of concern include crude oil, diesel fuel, gasoline, Therminol, glycol (ethylene and propylene), methanol, drilling fluids, produced water, and seawater. In tundra communities, diesel, gasoline, and sewage spills to tundra are the primary potential concerns. Other substances, such as hazardous wastes, may be spilled on tundra but would usually be spilled in small quantities and could require development of spill-specific treatment regimes.

It should be noted that in a typical spill in oil-producing areas, more than one substance may be released. A typical example would be a release of saline water and crude oil.

CRUDE OIL

Crude oil is a substance of fossil, biogenic origin, which contains thousands of organic and a few inorganic compounds. Included in crude oil are natural gas, liquefied petroleum oils, resins, and asphaltenes. Hydrocarbons, which are composed only of carbon and hydrogen atoms, are the most abundant components of crude oil. Other components include sulfur, oxygen, nitrogen, and a variety of metals which are bound to organic compounds or exist as inorganic salts.

The composition of crude oil determines its behavior and fate when spilled onto the tundra. It also affects the responses of tundra vegetation to oiling. Crude oil can kill plants in several ways. The light fractions of the crude oil, consisting of short-chain and aromatic hydrocarbons, cause the most severe damage to plants by penetrating and destroying the plant tissues. If the affected plant tissues are necessary to the plant's survival, the plant could be killed. Otherwise, the plant may survive with reduced biomass and vigor. Heavier fractions of crude oil can coat the surface of the leaves and prevent gas exchange, which is necessary for normal plant function. The plant may be killed if enough leaf or stem tissue is oiled.

Crude oil can also damage vegetation indirectly by creating hydrophobic (unwettable) soil conditions (Walker et al., 1978; McKendrick, 1999). Plants, particularly those in moist and **wet tundra**, require substantial amounts of soil moisture and are unable to survive such conditions. Crude oil can also displace the air occupying pore spaces in **dry or moist tundra** and cause the soil to become anaerobic. Moreover, the added organic carbon in the form of crude oil can stimulate microorganisms to decompose the oil, which can deprive higher plants of nutrients (McKendrick, 1999).

Several factors influence the toxic and physical effects of crude oil on tundra vegetation, including season that the spill occurs, weathering, and soil properties. For example, if the oil is perched on top of frozen or water-saturated soils, the most toxic aromatic fractions will evaporate and may not penetrate the soil (McKendrick, 1999). This is especially important for sedges and grasses — common plants in tundra — because the perennating buds lie below ground and can escape the most damaging components of crude oil when the oil does not penetrate the surface because the ground is frozen or water-saturated (Everett, 1978). Bark provides some protection for stems of shrubs, and their perennating buds are elevated above the soil surface, allowing them to escape damage if the oil has spread in a thin layer across the soil surface. **Dry tundra habitats are thought to be more susceptible to crude oil damage because the aromatic fractions can be carried into the soil before they evaporate, becoming trapped where roots and perennating buds can be killed (McKendrick, 1999).** Crude oil does not appear to be toxic to tundra vegetation at total petroleum hydrocarbon (TPH) levels of less than 13,000 mg/kg (Burgess et al., 1995, Cater and Jorgenson, 1999).

Despite the acute short-term adverse effects of crude oil on tundra vegetation, notable recovery has been documented in long-term observations of oiled sites (McKendrick, 1999). In an experiment on North Slope, wet tundra coated with crude oil at a rate of 250 barrels per acre (corresponding to a thickness of about 10 mm or about 3/8 inch) showed nearly complete natural revegetation with native species after 24 years without cleanup or treatment. However, crude oil applications of 1,000 barrels per acre (thickness 40 mm or about 1.5 inches) to wet tundra inhibited revegetation substantially. Even after 24 years, these areas had less vegetation cover and fewer species than nearby unoiled areas (McKendrick, 1999). In general, vascular

Conversion Table for Oiling Rates, Surface Thickness, and Soil Concentrations of Crude

SURFACE OILING RATE				SURFACE THICKNESS		PERCENT OIL IN SOIL BY VOLUME		PERCENT BY DRY WEIGHT (soil bulk density = 0.4)		PARTS PER MILLION (ppm; mg/kg) DW	
liters/ m^2	quarts /yd^2	gallons /acre	bbl /acre	mm	inches	Soil Oiling Depth (cm)		Soil Oiling Depth (cm)		Soil Oiling Depth (cm)	
						10	5	10	5	10	5
10	2 1/4	10691	255	10	3/8	10	20	22	44	220000	440000
5	1	5346	127	5	3/16	5	10	11	22	110000	220000
1	1/4	1069	25	1	1/16	1	2	2.2	4.4	22000	44000
0.1	-	107	3	0.1	-	0.1	0.2	0.22	0.44	2200	4400

plant cover observe 24 years after experimental oiling decreased with increasing experimental oil-application rates. These results correspond well with findings by Cater and Jorgenson (1999), who compared relationships between soil hydrocarbon concentrations and vegetation cover among several accidental crude-oil spill sites on wet tundra on the North Slope. The following conversion table presents oiling rates (volume units/area units) in terms of petroleum hydrocarbon concentrations (part per million (ppm) or milligrams per kilogram (mg/kg) in soil.

In general, shrubs, mosses and forbs have been shown to be more sensitive to crude oil than have grasses and sedges (Walker et al., 1978; Jorgenson and Cater, 1992). However, trampling and heavy equipment use for spill response can also cause considerable damage to the tundra. The possible damage done by responding needs to be weighed against the benefits of additional crude oil removal.

The initial spill response strategy for crude oil spills to tundra should be to prevent further spread of the oil, to prevent wildlife injury and to recover as much free product as possible. Rapid spill response is necessary to prevent the penetration of crude oil into the tundra soil which may result in the injury of plant roots and perennating buds. Water-saturated soils help to minimize soil penetration of petroleum into wet tundra, but moist and dry tundra are much more susceptible to soil penetration due to less soil moisture and greater soil pore space.

It is possible to recover more of the crude oil without injury in tundra when the spill occurs when soils are frozen and snow is present. Frozen soils help to prevent soil penetration and snow can act as an adsorbent, limiting lateral spread. Further advantages for winter spill response are that use of heavy equipment and foot traffic are less damaging to tundra, plants are dormant and wildlife is less prevalent. Winter spill response to crude oil spills may include vacuuming, scraping up crude-saturated snow and ice, flooding and skimming. While winter crude oil spills may be effectively cleaned up with little soil penetration, responses to crude oil spills in summer are more difficult. Summer spill response is problematic because of greater wildlife presence, increased difficulty in accessing the site and performing work without trampling the tundra, and lack of a frozen layer to prevent vertical migration. Summer spill response tactics for crude oil spills usually include vacuuming and skimming free product and using flooding and flushing to lift crude oil from the tundra soil and plants.

Burning can be a useful tool to remove residual crude oil from the soil surface or from vegetation following the use of other tactics to remove the majority of crude oil. **Permission from the ADEC project manager for the spill must be granted prior to burning.** Burning is not a good option for dry tundra because of the likelihood of burning soil organic matter and because perennating buds of many species in dry tundra occur above ground where they are susceptible to fire damage.

DIESEL FUEL

Diesel, which is a petroleum product refined from crude oil, is composed of many different chemicals. When the fuel is spilled on tundra, the volatile diesel components (aromatic hydrocarbons such as benzene) evaporate, changing the chemical composition of the spill. Other chemicals in the fuel will dissolve into active-layer water or surface water, while some chemicals such as polynuclear aromatic hydrocarbons (PAHs) may adsorb to fine particles in tundra soil and persist for a long time. Soil microbes that degrade the hydrocarbons may be unable to metabolize the adsorbed PAH molecules, and biodegradation is inhibited. However, the soil adsorption of PAH molecules can reduce phytotoxicity, since adsorbed chemicals are not available for plant uptake.

Diesel spills to tundra are generally more damaging to soil and vegetation than spills of crude oil (Walker et al., 1978; Jorgenson and Cater, 1996). Diesel range organics (DRO) levels of 1,000 - 2,000 mg/kg were found to inhibit seed germination and plant growth (Cater et al., 1997). DRO levels of 1,600 and 2,800 mg/kg were found where vegetation was stressed or dead where diesel was spilled at Wainwright, Alaska (Woodward-Clyde, 1995a, 1995b). Lawson et al. (1978) examined several sites on the National Petroleum Reserve 28 years after a diesel spill and found that little vegetation recovery had occurred.

Direct exposure of plant leaves to diesel will kill the leaves and can kill the entire plant if roots and perennating buds are also exposed. Diesel spills to dry or moist tundra are potentially more damaging to tundra vegetation than is a similar spill to wet tundra. The water-saturated root zone of wet tundra may confer initial soil protection, though the presence of water-soluble hydrocarbons like napthalene in diesel results in eventual penetration of these toxic fractions into the soil and subsequent plant injury.

Rapid response to diesel spills is critical to minimizing surface and vertical migration in tundra. Containment and product recovery must be completed as soon as possible after the spill. In winter, snow and ice help to contain diesel spills and minimize soil penetration with the result that many winter spills have been cleaned up with no damage to tundra. However, a review of summer diesel spills (AMEC, 2001) showed that summer diesel spills to tundra always produced vegetation injury. Flooding and flushing, raking, and cutting of diesel-coated vegetation may be used to remove residual diesel contamination. Prior to burning, permission must be granted by the ADEC project manager handling the spill. Soil aeration, water management, fertilization and revegetation are useful long-term remediation tactics for diesel spills.

GASOLINE

Gasoline is highly volatile and flammable refined petroleum product that spreads rapidly to a thin sheen on water or wet soil. Evaporation rates are very high; gasoline contains a larger percentage of volatile aromatic compounds than either diesel or crude oil.

Gasoline spills on tundra are generally more damaging to soil and vegetation than spills of crude oil. Direct contact of plant leaves with gasoline will often kill the entire plant. Some **wet tundra** vegetation may be initially resistant to gasoline spills where interstitial water protects the root zone; however, like diesel, gasoline has water-soluble fractions which may migrate into the root mat and organic soils in a relatively short time. **Moist and dry tundra** are highly susceptible to the effects of gasoline spills for the same reasons they are susceptible to the effects of diesel spills—rapid penetration of the soil and trapping of the toxic aromatic fractions in the root zone, where they can be toxic to vegetation. Depending on incident-specific and site-specific conditions, overall phytotoxic effects of diesel may be higher than those of gasoline. Many of the harmful aromatic fractions of gasoline may evaporate before penetrating tundra soils.

SALINE WATERS AND SUBSTANCES

Seawater and brine are used on the North Slope as part of enhanced oil recovery processes and are transported via pipeline and truck. Produced water is generally separated from the oil stream and reinjected at well heads. Fire-fighting chemicals also contain salts and cause similar effects to tundra vegetation.

High levels of sodium and chloride ions in saline spills increase the osmotic potential of soil water, making water uptake more difficult or impossible for non-salt-tolerant tundra plants. Depending on spill concentrations, salt-impacted vegetation may wilt, become discolored, drop leaves, or die within hours or days of contact with foliage or roots (Barker, 1985). Saline substances spread rapidly on **wet and moist tundra**, and newly affected areas may become apparent with each growing season as the spill spreads (Barker, 1985; Reiley et al., 1995). Jorgenson et al. (1987) found that damage to tundra vegetation was moderate at soil salinity levels of 2-3 mmhos/cm and severe at 6-10 mmhos/cm. Simmons et al. (1983) made controlled releases of seawater to tundra at 8 sites in the Prudhoe Bay, Alaska area. They found that live plant cover was reduced by 61 to 87% in dry and moist tundra sites.

Crude oil is often a part of saline water spills, and the emphasis on cleanup has been directed more at cleaning up the crude than the saline water. However, the salts affect vegetation at much lower levels, and the effects are usually longer lasting since salts do not bioattenuate. Thus more of the emphasis on cleanup of mixed saline water and crude spills should be placed on cleanup of the saline water.

Initial spill response for spills of saline substances should include containment and removal of salt water. Repeated flooding and water recovery has been found to be an effective tactic for removing residual salts. Long-term remediation tactics that may have potential are addition of gypsum (Cater and Jorgenson, 1995) and planting of salt-tolerant plant species.

DRILLING MUDS AND FLUIDS

Drilling muds and fluids consist of a complex and variable mixture to meet oil-well drilling needs and usually contain bentonite clay, saline substances and heavy metals. Tundra vegetation and aquatic invertebrate communities in Alaska and Canada have been damaged by drilling muds leaking from reserve pits that are used to store drilling muds. Spills of drilling fluids to tundra have also resulted from well blowouts. Drilling mud spills are usually accompanied by varying amounts of crude oil and saline water.

The salinity of drilling muds and smothering due to burial appear to be the primary factors associated with toxicity of drilling muds to tundra plants (McKendrick, 1986; Railton, 1975; Jorgenson and Kidd, 1994; Burgess et al., 1997). Railton (1975) found that plant recolonization decreased with increasing thickness of drilling mud deposits. Little plant growth occurred on drilling mud deposits six inches deep. Tussock grass (*Eriophorum vaginatum*) and woody plants survive these spills better than other plants because they are not totally buried. The salinity effects of drilling muds appear to be caused by high levels of sodium whereas salinity effects of produced water or seawater are caused more by high chloride levels (Burgess et al., 1997).

For spills that occur during winter, careful removal of frozen drilling muds to within 1 to 2 inches of the soil surface followed by vacuuming appears to be an effective cleanup tactic. Flushing and subsequent water removal may also be warranted.

SYNTHETIC FLUIDS

Methanol. Also known as wood alcohol or methyl alcohol, methanol is a highly flammable, volatile solvent used in oil field operations. Methanol is a clear, colorless liquid with a pungent odor, is completely soluble in water, and is expected to degrade quickly in both soil and water (estimated half-life is between 1 to 10 days [J.T. Baker MSDS]). Methanol evaporates quickly from soil and water when exposed to air. This chemical is highly toxic to wildlife, but its toxicity to plants is not well known. Following a winter spill on the Alaska North Slope, methanol levels in soil of 4,300 mg/kg were measured after initial cleanup. Little damage to tundra was found the following spring, but the methanol may have been diluted by spring snow melt and evaporation (Cater et al., 1998). The toxic effects of methanol may be reduced by dilution with water or by evaporation.

Initial spill response for methanol spills should focus on wildlife protection and then containment and recovery.

Glycols. Ethylene and propylene glycol are synthetic liquids that absorb water. They are used as antifreeze for vehicles, and are used in heating systems and in industrial applications. Glycols are clear, odorless liquids that are miscible with water and have low vapor pressures. When released into the environment, glycols have short half-lives (3 to 10 days at warm temperatures) and may be biodegraded by microorganisms (Howard, 1991). Abiotic transformations in soil or water are not significant except that glycols are subject to photo-oxidation. There is no information on the toxicity of glycols to plants. Ethylene glycol is highly toxic to animals, so initial response to spills of this compound should focus on wildlife protection, followed by containment and recovery.

Standard containment and product recovery tactics followed by flooding and water/glycol recovery are standards for glycol spill response on tundra.

Therminol. An insoluble organic liquid, therminol (Therminol 59) is commonly used as a heat transfer fluid for pump stations and well houses. In its raw form, it is a clear yellow liquid exhibiting a mild hydrocarbon odor and is viscous even in below-freezing temperatures. Little is known about the environmental toxicity of therminol. Biodegradation tests suggest that it is resistant to biodegradation (Solutia MSDS). No long-term studies have been made regarding the effects of therminol spills in tundra. Because the toxicity of therminol is not known, high removal rates should be adhered to following a spill. Standard containment and product recovery techniques followed by flooding and further product removal are recommended tactics.